

Reactions of FeCH₂⁺ and CoCH₂⁺ with Cyclic Alkanes in the Gas Phase

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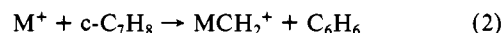
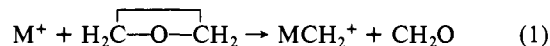
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Abstract: Gas-phase reactions of the title carbenes with cyclic alkanes with use of Fourier transform mass spectrometry (FTMS) are described. The metal-carbene reacts with both cyclopropane and cyclobutane by initial C-C bond insertion. The methyldiene-metallacyclobutane species produced from cyclopropane appears to decompose by three pathways: (1) cleavage of the metallacyclobutane ring (olefin metathesis), (2) ring expansion by carbene/alkyl coupling, and (3) β-hydride abstraction. With cyclobutane, an MC₅H₆⁺ ion is produced which consists of cyclopentadiene bound to the metal ion. For cyclopentane and cyclohexane, initial insertion into C-H bonds dominates generating M(cyclic olefin)⁺ species. Small amounts of M(C₆H₈)⁺ and M(C₇H₈)⁺ were also produced from cyclopentane and cyclohexane, respectively, and are assigned as M(MCP)⁺ (MCP = methylcyclopentadiene) and M(tol)⁺ (tol = toluene).

The formation and fragmentation of metallacycles is important in organotransition-metal chemistry since these processes are involved in a number of key catalytic transformations. Olefin metathesis,¹⁻³ hydrocarbon cracking and isomerization,⁴ epoxidation,⁵ and deepoxidation⁶ are all believed to proceed through the intermediacy of metallacyclobutanes. Metallacyclopentanes appear to be intermediates in a variety of olefin dimerization reactions.^{7,8} Metal carbenes⁹ represent another class of compounds important to the field of organotransition-metal chemistry and have been implicated as intermediates in olefin metathesis,¹⁻³ polymerization of olefins,¹⁰ cyclopropane formation from olefins,¹¹ olefin homologation,¹² and metal-alkyl decompositions.¹³ Studying the decomposition pathways of metallacycles as well as the chemistry of transition metal carbenes, therefore, may provide insight into catalytic pathways. Significant ligand and solvent effects are seen in these processes. For example, the mechanism of decomposition of nickelacyclopentanes in solution is strongly dependent on the coordination state of the metal.^{14,15}

Studies involving metallacyclic species and metal carbenes in the gas phase are particularly interesting since no solvent molecules are present. Recently, reactions of the first-row group-8 transition-metal (Fe, Co, Ni) ions with cyclic alkanes were studied^{16,17} with both dehydrogenation and ring cleavage observed. Dehydrogenation proceeds with retention of the ring's integrity.¹⁷ Ring cleavage was proposed to proceed through metallacyclic intermediates.^{16,17} Stable metallacyclobutane^{17b} and metallacyclopentane^{17,18} ions were generated by decarbonylation of cyclobutanone and cyclopentanone, respectively, and their decomposition processes studied.

Naked iron and cobalt carbene ions are produced from both ethylene oxide¹⁹ and cycloheptatriene,²⁰ reactions 1 and 2.



Reactions of FeCH₂⁺ and CoCH₂⁺ with olefins²³ and aliphatic alkanes²⁴ have been studied in detail in the gas phase. Summarizing this work, reactions with simple olefins were dominated by metathesis products²³ while these metal carbenes were found to react with aliphatic alkanes predominantly by C-H bond insertion in contrast to the corresponding atomic metal ions which prefer C-C bond insertions.^{18,25}

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- (20) This reaction was first reported for Co⁺: Jacobson, D. B.; Byrd, G. D.; Freiser, B. S. *Inorg. Chem.* **1984**, *23*, 553. With use of the bond energies in ref 21 and the heats of formation in ref 22, formation of FeCH₂⁺ and CoCH₂⁺ from cycloheptatriene is calculated to be exothermic by 29 ± 5 and 16 ± 7 kcal/mol, respectively, assuming benzene as the neutral product.

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Table I. Distribution of Neutral(s) Lost in the Reaction of FeCH_2^+ and CoCH_2^+ with Cyclic Alkanes^a

cyclic alkane	carbene	neutral(s) lost													
		H_2	2H_2	3H_2	CH_4	$\text{CH}_4 + \text{H}_2$	$\text{CH}_4 + 2\text{H}_2$	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_5H_{10}	C_6H_{12}	C_7H_{14}
\triangle	FeCH_2^+	8						67				25			
	CoCH_2^+	33						35				32			
\square	FeCH_2^+		10		6			26		21			37		
	CoCH_2^+		18		18			24		13			27		
pentagon	FeCH_2^+		3			82								15	
	CoCH_2^+		10			78			2	6				4	
hexagon	FeCH_2^+			2		6	80								12
	CoCH_2^+			8	2	23	60				3	2			2

^aProduct distribution reproducible to $\pm 10\%$.

Here, we study in detail the reactions of FeCH_2^+ and CoCH_2^+ with cyclic alkanes using Fourier transform mass spectrometry (FTMS). NiCH_2^+ was not studied due to the difficulty in generating it in sufficient quantities. Structures of product ions were probed by collision-induced dissociation (CID),²⁶ specific ion-molecule reactions, and H/D exchanges using deuterium.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectroscopy²⁷ and Fourier transform mass spectrometry (FTMS)²⁸ have been discussed elsewhere. All experiments were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail²⁹ and equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and utilizes 80% neutral density screens as the transmitter plates which permit irradiation with various light sources. High-purity foils of the appropriate metals were attached to the opposite transmitter screen. Metal ions are generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto a metal foil. Details of the laser ionization technique have been described elsewhere.³⁰

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove non-condensable gases. $\text{C}_2\text{D}_4\text{O}$ (>98 atom % D) was obtained from MSD Isotopes, Merck Chemical Division. Sample pressures were on the order of 1×10^{-7} torr. Argon was used as the collision gas for the collision-induced dissociation (CID) experiments at a pressure of approximately 5×10^{-6} torr. A Bayard-Alpert ionization gauge was used to monitor pressure.

Details of the CID experiments have previously been discussed.^{18,29,31,32} The collision energy of the ions can be varied (typically between 0 and 100 eV) from which plots of CID product ion intensities vs. kinetic energy can be made. These plots are reproducible to $\pm 5\%$ absolute and yield additional structural information. The spread of ion kinetic energies is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.³³

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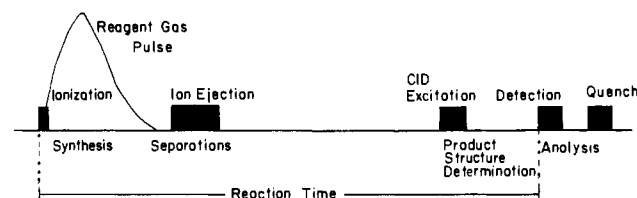
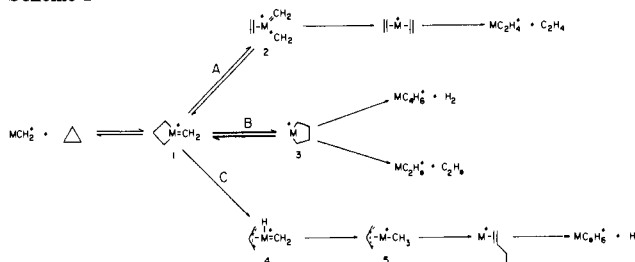


Figure 1. Sequence of events for pulsed valve addition of reagent gas for the FTMS experiment. See Experimental Section for a more detailed explanation.

Scheme I



The MCH_2^+ ions were generated by reacting laser desorbed Fe^+ and Co^+ with ethylene oxide¹⁹ or cycloheptatriene,²⁰ reactions 1 and 2. The carbenes generated in reactions 1 and 2 gave identical results (within experimental error) for reactions with the cyclic alkanes, Table I. Furthermore, the addition of a high pressure of argon ($\sim 5 \times 10^{-6}$ torr) had little effect on the product distributions in Table I. This suggests that the M(R)^+ ($\text{R} = \text{carbene}$) ions formed in reactions 1 and 2 contain little excess internal energy. Labeled carbene (MCD_2^+) was formed by reaction with deuterated ethylene oxide. The carbene reagent gas (ethylene oxide or cycloheptatriene) was introduced into the vacuum chamber through a General Valve Corp. series 9 pulsed solenoid valve.³⁴ The sequence of events with use of the pulsed valve for addition of a reagent gas is illustrated in Figure 1. Initially, a concurrent laser (metal ionization) and valve pulse occurs. The pulsed reagent gas fills the vacuum chamber to a maximum pressure of $\sim 10^{-5}$ torr and is pumped away by a high-speed 5-in. diffusion pump in ~ 250 ms. The MCH_2^+ (MCD_2^+) ions are then isolated by swept double resonance ejection techniques²⁸ and allowed to react with a static pressure of a reagent gas without complicating reactions with ethylene oxide or cycloheptatriene. The products resulting from reactions with the static reagent gas can be isolated by additional swept ejection pulses to allow their further chemistry to be studied or their CID spectra to be obtained. The distributions of neutral(s) lost in the primary reactions of MCH_2^+ and MCD_2^+ are summarized in Tables I and II, respectively.

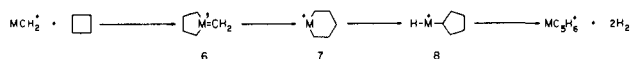
Results and Discussion

Cyclopropane. Cyclopropane yields three products with FeCH_2^+ and CoCH_2^+ , reactions 3–5. The ratio for dehydrogenation, reaction 5, with MCD_2^+ for total scrambling is 15:12:1 for

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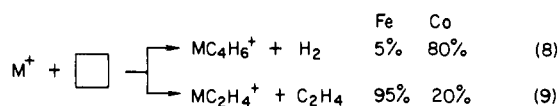
(34) A detailed description of pulsed valve introduction of reagent gases in conjunction with FTMS can be found in Carlin and Freiser: Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

Scheme II



alkyl/carbonyl migratory insertions.⁴⁵

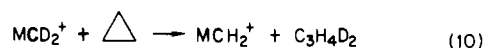
Metallacyclopentanes decompose in solution by symmetric ring cleavage resulting in formation of ethene, by β -hydride elimination producing butene and by reductive elimination of cyclobutane-1,3c,14,15,46-48. Stable metallacyclopentane ions have been synthesized in the gas phase by decarbonylation of cyclopentanone^{17,15} by Fe^+ and Ni^+ . These metallacyclopentane ions decompose upon collisional activation both by symmetric ring cleavage (C_2H_4 elimination) and by dehydrogenation. Labeling studies in the gas phase indicated that symmetric ring cleavage occurred with no H/D scrambling; however, dehydrogenation proceeded with considerable scrambling.¹⁷ Absence of H/D scrambling for symmetric ring cleavage indicates that H/D scrambling occurs only after rearrangement to a structure different than metallacyclopentane, presumably a linear butene complex.⁴⁹ Finally, Fe^+ ¹⁷ and Co^+ ^{16,17} react with cyclobutane, yielding the products in reactions 8 and 9. These reactions are proposed to proceed



through metallacyclopentane intermediates and suggest that dehydrogenation is much more facile for cobaltacyclopentane ions than for ferracyclopentane ions.

Dehydrogenation may also proceed by β -hydride abstraction from **1** (route C, Scheme I). Rearrangement of metallacyclopentanes to metal olefin complexes via hydride- π -allyl intermediates has been proposed in solution-phase studies.^{38,50,51} β -Hydride abstraction is followed by formation of a methyl-allyl intermediate **5**. C-C bond formation generates an activated linear butene complex which can undergo considerable H/D scrambling prior to dehydrogenation.⁴⁹ Dehydrogenation by route C is probably more likely to occur for cobalt than for iron since cobaltacyclobutane ions readily rearrange to $\text{Co}(\text{prop})^+$ (prop = propene) in the gas phase and ferracyclobutane ions do not.^{17b,52}

Finally, the thermoneutral reaction 10 occurs for FeCD_2^+ but not for CoCD_2^+ . This probably proceeds via an equilibrium



between species **1** and **2** in Scheme I with reductive elimination of cyclopropane from **1**. Observation of reaction 10 implies that rearrangement of the bis(methylidene)-ethene complex, **2**, to the methylidene-metallacyclobutane species, **1**, is competitive with methylene coupling of intermediate **2** forming $\text{M}(\text{eth})_2^+$ (eth = ethene) for iron. Alternatively, species **1** and **3** in Scheme I may be in equilibrium. There is strong evidence that a nickelacyclohexane complex undergoes α -C-C bond cleavage forming a

(45) For a general review of CO insertion reactions see: Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

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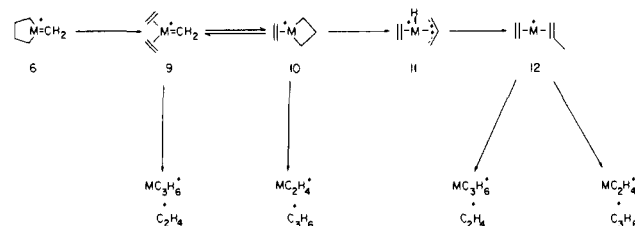
(49) Considerable H/D scrambling occurs for reaction of Fe^+ and Co^+ with 1-butene-1,1- d_2 in the gas phase, presumably proceeding through the interconversion of hydrido- π -allyl and linear butene-metal ion species. See for example ref 32.

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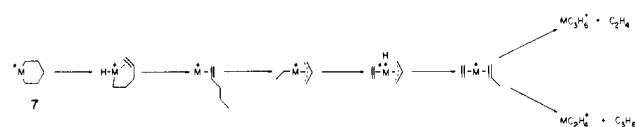
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Scheme III



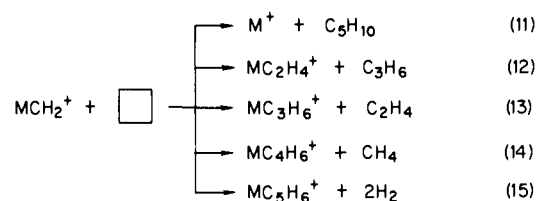
Scheme IV



methylidene-metallacyclopentane species in solution.⁵³

Formation of the bare metal ions (elimination of C_4H_8) may proceed by reductive elimination of cyclobutane or linear butene. Elimination of butadiene + H_2 or two ethenes are both thermally unfavorable.⁵⁴

Cyclobutane. Both FeCH_2^+ and CoCH_2^+ yield five products with cyclobutane, reactions 11-15. The product of reaction 15,



MC_5H_6^+ , yields elimination of C_5H_6 as the only fragmentation upon collisional activation. In addition, this product undergoes six H/D exchanges with D_2 . These results are indicative of $\text{M}(\text{CP})^+$ (CP = cyclopentadiene) species.¹⁷ A mechanism for formation of $\text{M-c-C}_5\text{H}_6^+$ in reaction 15 is outlined in Scheme II. Initially, the carbene oxidatively inserts into a C-C bond of cyclobutane generating an activated methylidene-metallacyclopentane species **6**. Incorporation of methylene into the metallacyclic ring generates the ring-expansion product **7** followed by rearrangement to a hydrido-cyclopentyl complex **8** which eliminates 2H_2 forming $\text{M-c-C}_5\text{H}_6^+$. The reverse of the above ring expansion process (α -C-C bond cleavage) has been observed for nickelacyclohexanes in solution.⁵³ Roughly equal amounts of 2H_2 and $\text{H}_2 + \text{HD}$ elimination are observed with MCD_2^+ , Table II. Observation of this ring-expansion process for cyclobutane lends support to the ring expansion described above for cyclopropane.

Methane elimination, reaction 14, probably proceed by two sequential β -hydride shifts from intermediate **6** forming $\text{M}(\text{but})^+$ (but = butadiene). CID on the product of reaction 14 yields C_4H_6 elimination as the only fragmentation consistent with $\text{M}(\text{but})^+$ species.³²

Elimination of C_3H_6 and C_2H_4 , reactions 12 and 13, corresponds to C-C bond cleavage of the cyclobutane ring. With MCD_2^+ , elimination of C_2H_4 and $\text{C}_3\text{H}_4\text{D}_2$ dominates with considerable scrambling seen for cobalt, Table II. A mechanism for these losses is presented in Scheme III. Irreversible symmetric ring cleavage of **6** generates the bis(ethene)-methylidene complex **9**.⁵⁵ Intermediate **9** can eliminate C_2H_4 or rearrange to an ethene-me-

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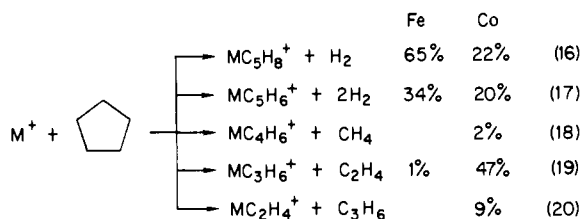
(54) Elimination of $2\text{C}_2\text{H}_4$ is endothermic by 15.8 kcal/mol for FeCH_2^+ and 4.8 kcal/mol for CoCH_2^+ with butadiene + H_2 also endothermic by 17.2 kcal/mol for FeCH_2^+ and 6.2 kcal/mol for CoCH_2^+ . Elimination of 1-butene is exothermic by 9.1 kcal/mol for FeCH_2^+ and 20.1 kcal/mol for CoCH_2^+ and cyclobutane elimination is also exothermic by 2.8 kcal/mol for FeCH_2^+ and 13.8 kcal/mol for CoCH_2^+ . These calculations use the bond energies in ref 21 and the heats of formation in ref 22.

(55) Symmetric ring cleavage of ferracyclopentane and cobaltacyclopentane ions to form bis(ethene) complexes is irreversible in the gas phase. See for example ref 17.

tallacyclobutane species **10**. Intermediate **10** can reductively eliminate cyclopropane⁵⁶ as well as undergo interconversion with intermediates **9** and **11**. Complex **11** can readily rearrange to the bis(olefin) species **12**, which can eliminate either C_2H_4 or C_3H_6 .

Roughly equal amounts of C_2H_4 and C_3H_6 elimination occur for FeCH_2^+ . This suggests that these eliminations probably proceed predominantly from intermediates **9** and **10** instead of from **12**. Conversion to intermediate **12** would result in considerably more C_2H_4 elimination than C_3H_6 ^{18,32,57} since smaller olefins are bound more weakly than larger olefins to cationic metal centers in the gas phase and, therefore, the smaller olefin will be preferentially cleaved.⁵⁸ For CoCH_2^+ the ratio of C_2H_4 to C_3H_6 elimination is roughly 2:1. Furthermore, considerable H/D scrambling is observed with CoCD_2^+ . This scrambling can be rationalized by invoking reversible β -hydride shifts in **12** prior to olefin elimination.⁵⁹

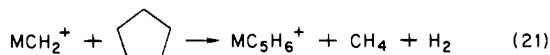
Fe^+ and Co^+ react with cyclopentane to yield the products in reactions 16–20.^{16,17} The C–C bond cleavages, reactions 18–20,



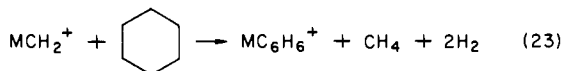
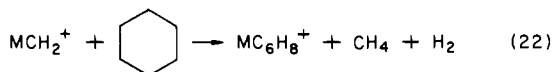
are believed to proceed by initial formation of an activated metallacyclohexane intermediate **7** which subsequently rearranges to a $\text{M}(1\text{-pent})^+$ (pent = pentene) species via a 1–4 hydrogen atom shift¹⁷ which ultimately decomposes predominantly by insertion into an allylic C–C bond, Scheme IV.^{18,32,57} This mechanism predicts formation of $\text{M}(\text{C}_5\text{H}_4)(\text{C}_3\text{H}_4\text{D}_2)^+$ (50%), $\text{M}(\text{C}_2\text{H}_2\text{D}_2)(\text{C}_3\text{H}_6)^+$ (17%), and $\text{M}(\text{C}_2\text{H}_3\text{D})(\text{C}_3\text{H}_5\text{D})^+$ (33%) which should decompose, yielding products with varying amounts of deuterium due to H/D scrambling prior to olefin elimination.⁵⁹ This is clearly not seen for iron carbene; however, some scrambling is seen for cobalt carbene. Therefore, the C–C bond cleavages appear to proceed predominantly by Scheme III with some also occurring by Scheme IV for cobalt carbene.

Formation of Co^+ in reaction 11 by elimination of cyclopentane, cyclopentene + H_2 , and butadiene + methane is exothermic while formation of Fe^+ in reaction 11 is only exothermic for elimination of cyclopentane.⁶⁰

Cyclopentane and Cyclohexane. The neutral losses for the reactions of cyclopentane and cyclohexane with MCH_2^+ and MCD_2^+ are dominated by retention of the ring's integrity in contrast to the smaller cyclic alkanes where ring cleavages dominate. Structural studies indicate that $\text{M-c-C}_5\text{H}_6^+$ is generated in reaction 21 and that $\text{M-c-C}_6\text{H}_8^+$ and $\text{M-c-C}_6\text{H}_6^+$ are formed

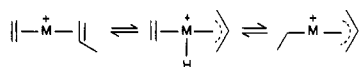


in reactions 22 and 23. Similar behavior has been observed for



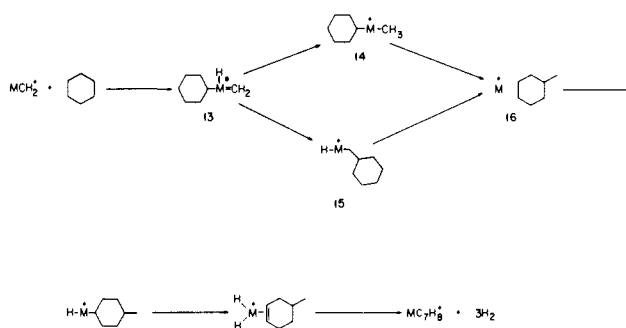
reactions of the bare transition-metal ions (Fe^+ and Co^+) with

(56) Grubbs, R. H. *Inorg. Chem.* **1979**, *18*, 2623.
 (57) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624.
 (58) Kappes, M. M.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1813.
 (59) The following equilibrium has been observed for Fe^+ , Co^+ , and Ni^+ in the gas phase. See ref 52.



(60) On the basis of the bond energies in ref 21 and heats of formation in ref 22.

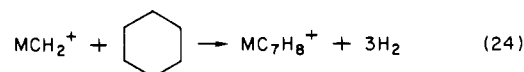
Scheme V



cyclic alkanes where ring cleavages dominate for cyclobutane while cyclopentane and cyclohexane predominantly yield retention of the ring's integrity.^{16,17,61} This difference in chemistry for larger cyclic alkanes is attributed to the relatively weak C–H bonds (94.5 ± 1 kcal/mol for cyclopentane and 95.5 ± 1 kcal/mol for cyclohexane)^{35b} and the fact that the C–C bonds have little or no strain energy.

A small amount of C–C bond cleavage occurs for CoCH_2^+ with cyclopentane and cyclohexane, but none occurs for FeCH_2^+ . These cleavages probably result from initial insertion into a C–C bond generating an activated methyldene–metallacyclic species which subsequently decomposes. The mode of decomposition of these activated methyldene–metallacyclic complexes is probably quite complex with several decomposition channels available.

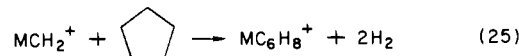
As with cyclopropane and cyclobutane, dehydrogenation products are also observed for cyclopentane and cyclohexane. Reaction with cyclohexane yields only one dehydrogenation product, reaction 24. Complete retention of the label is seen for



MCD_2^+ . Collisional activation of CoC_7H_8^+ yields only C_7H_8 elimination. The FeC_7H_8^+ intensity was too low to allow for it to be studied. $\text{M}(\text{tol})^+$ yields elimination of C_7H_8 as the only fragmentation upon collisional activation. CID of authentic $\text{M}(\text{CH})^+$ (CH = cycloheptatriene) and $\text{M}(\text{NB})^+$ (NB = norbornadiene) species ($\text{M} = \text{Fe}, \text{Co}$) yield elimination of C_2H_2 , C_3H_6 , C_6H_6 , and C_7H_8 . In addition, some H· elimination from $\text{Fe}(\text{CH})^+$ is also observed. These results are consistent with formation of $\text{M}(\text{tol})^+$ in reaction 24.

A mechanism for formation of $\text{M}(\text{tol})^+$ in reaction 24 is presented in Scheme V and involves initial oxidative addition across a C–H bond forming **13**. Intermediate **13** rearranges to **14** and **15** which undergo reductive elimination forming a metal ion–methylcyclohexane species **16**. Oxidative addition across a C–H bond is followed by elimination of 3H_2 forming $\text{M}(\text{tol})^+$. This mechanism also predicts retention of the label with MCD_2^+ . In addition to elimination of 3H_2 , intermediate **16** may also lose methane forming $\text{M}(\text{CH})$ (CH = cyclohexene) which can undergo subsequent dehydrogenations.^{17a}

Dehydrogenation of cyclopentane by MCH_2^+ yields MC_6H_8^+ , reaction 25, with complete retention of label observed for MCD_2^+ .



Again, the intensity of the iron analogue was too low for it to be studied. CID of CoC_6H_8^+ yields dehydrogenation forming CoC_6H_6^+ in high efficiency along with C_6H_8 elimination. $\text{CoC}_6\text{H}_6\text{D}_2^+$, generated from CoCD_2^+ , yields dehydrogenation by eliminating H_2 ($\sim 60\%$) and HD ($\sim 40\%$). These results are consistent with formation of $\text{M}(\text{MCP})^+$ (MCP = methylcyclopentadiene) in reaction 25 by a mechanism similar to that presented in Scheme V for MC_7H_8^+ formation from cyclohexane. Dehydrogenation of CoC_6H_8^+ would then generate $\text{Co}(\text{ful})^+$ (ful

(61) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565.

= fulvene) upon collisional activation.

Conclusions

FeCH_2^+ and CoCH_2^+ react with cyclopropane and cyclobutane exclusively by initial insertion across a C-C bond generating an activated methylenemetallic species which decomposes via a variety of pathways. There is good evidence for ring expansion via migratory insertion of methylene into the metallacyclic ring system. Methylene/alkyl coupling has been implicated in another study involving the reactions of MCH_2^+ ($\text{M} = \text{Fe}, \text{Co}$) with aliphatic alkanes,²⁴ and this process is well supported in solution chemistry.³⁸⁻⁴⁴ The ring-expansion product for reaction of MCH_2^+ with cyclobutane, reaction 15, generates M-c- C_5H_6^+ .

With cyclopentane and cyclohexane, retention of the ring's integrity dominates the reactions. This suggests initial attack of C-H bonds and not C-C bonds. The difference in reaction mechanisms between small and large cyclic alkanes is attributed to the strong C-H bonds in cyclopropane and cyclobutane coupled with C-C bonds weakened by strain energy. Therefore, these weak C-C bonds are preferentially attacked. The C-C bonds in cy-

clopentane and cyclohexane have little or no strain energy and, therefore, are not as susceptible to attack relative to the C-H bonds. Similar behavior has been observed for reactions of MCH_3^+ ($\text{M} = \text{Fe}$ and Co),⁶² $\text{Fe}^{+17,61}$, and $\text{Co}^{+16,17}$ with cyclic alkanes where cyclopropane and cyclobutane are dominated by ring cleavages while cyclopentane and cyclohexane are dominated by retention of the ring's integrity.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-AC02-80ER10689) for supporting this research and to the National Science Foundation (CHE-8310039) for supporting advances in FTMS methodology.

Registry No. FeCH_2^+ , 90143-30-9; CoCH_2^+ , 76792-07-9; H_2 , 1333-74-0; CH_4 , 74-82-8; C_2H_4 , 74-85-1; CH_2D_2 , 676-55-1; $\text{C}_2\text{H}_2\text{D}_2$, 29060-53-5; FeCD_2^+ , 93604-57-0; CoCD_2^+ , 93604-58-1; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7.

(62) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3900.

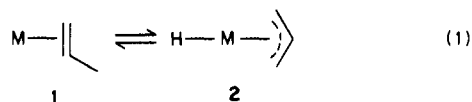
Dynamics of Monoolefin-Metal Ion Complexes in the Gas Phase. Determination of the Number of Labile Hydrogens by Reaction with C_2D_4

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Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received May 29, 1984

Abstract: H/D exchange reactions of organometallic ions with D_2 in the gas phase have proven valuable in determining the number of labile hydrogens in the complex. Unfortunately, many complexes are not observed to exchange with D_2 . In this paper we demonstrate that C_2D_4 can extend the variety of complexes which may be studied. The propene complexes of Fe^+ , Co^+ , and Ni^+ which are unreactive with D_2 undergo 5 H/D exchanges with C_2D_4 . These results are rationalized by invoking an equilibrium between the propene and hydrido- π -allyl species promoted by the activation afforded by ethene- d_4 coordination. The $\text{Rh}(\text{propene})^+$ complex is observed to exchange all 6 hydrogens suggesting an additional mechanism involving a vinylic C-H bond insertion. In addition, this $\text{Rh}(\text{propene})^+$ species undergoes multiple exchanges per C_2D_4 encounter in contrast to the $\text{M}(\text{propene})^+$ species of Fe^+ , Co^+ , and Ni^+ which undergo only a single exchange per C_2D_4 encounter. The rate of the above exchanges falls into the order $\text{Rh}^+ > \text{Co}^+ > \text{Fe}^+ > \text{Ni}^+$. $\text{Rh}(1,3\text{-pentadiene})^+$ undergoes 5 rapid exchanges with C_2D_4 while the corresponding iron and cobalt complexes yield 5 slow exchanges with no exchange observed for the nickel complex. No multiple exchanges occur for these pentadiene ions. The isomeric $\text{Rh}(2\text{-methylbutadiene})^+$ species undergoes 5 slow exchanges with none observed for the iron, cobalt, and nickel species. M-c- C_5H_6^+ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$) undergo 6 rapid exchanges with multiple exchanges predominating. The $\text{Rh-c-C}_5\text{H}_6^+$ species only undergoes one rapid exchange. Both $\text{Rh-c-C}_7\text{H}_8^+$ and $\text{Co-c-C}_7\text{H}_8^+$ generated from cycloheptatriene yield one slow exchange with C_2D_4 with none observed for $\text{Fe-c-C}_7\text{H}_8^+$ and $\text{Ni-c-C}_7\text{H}_8^+$.

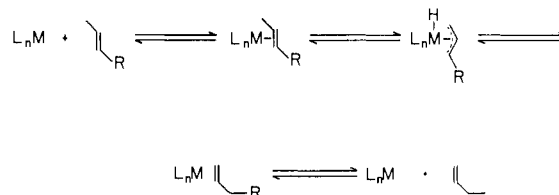
The ability of transition-metal complexes to effect structural transformations in organic substrates constitutes a basic facet of organometallic chemistry. One such transformation which has received much attention is the metal-promoted isomerization of olefins.¹ Under hydride-free conditions, reversible insertion into an allylic carbon-hydrogen bond has been frequently invoked as the mechanism for catalytic isomerization of olefins, Scheme I,² and is supported by detailed stereochemical studies.³⁻⁶ This mechanism is supported by detailed stereochemical studies.³⁻⁶ In addition, the hydrido- π -allyl intermediate has been observed directly,^{7,8} as well as in a dynamic equilibrium with the olefin complex,⁸⁻¹⁰ eq 1. Therefore, the mechanism presented in Scheme



I for the isomerization of olefins under hydride-free conditions has gained general acceptance.

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Scheme I



The above olefin isomerization requires that the metal complex contain an empty coordination site. An atomic transition metal

- (1) For reviews of transition-metal-catalyzed olefin isomerizations see: (a) Tolman, C. A. "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 271-312. (b) Hubert, A. J.; Reimlinger, H. *Synthesis* **1970**, 2, 405. (c) Davies, N. R. *Rev. Pure Appl. Chem.* **1967**, *17*, 83. (d) Orchin, M. *Adv. Catal. Rel. Subj.* **1966**, *16*, 1.
 (2) (a) Manuel, T. A. *J. Org. Chem.* **1962**, *27*, 3941. (b) Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 4591. (c) Harrod, J. F.; Chalk, A. *J. Am. Chem. Soc.* **1966**, *88*, 3491.
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